

MECHANISTIC INSIGHTS INTO SUPRAMOLECULAR CATALYSIS: CAPSULE-MEDIATED ARENE ALLYLATIONS

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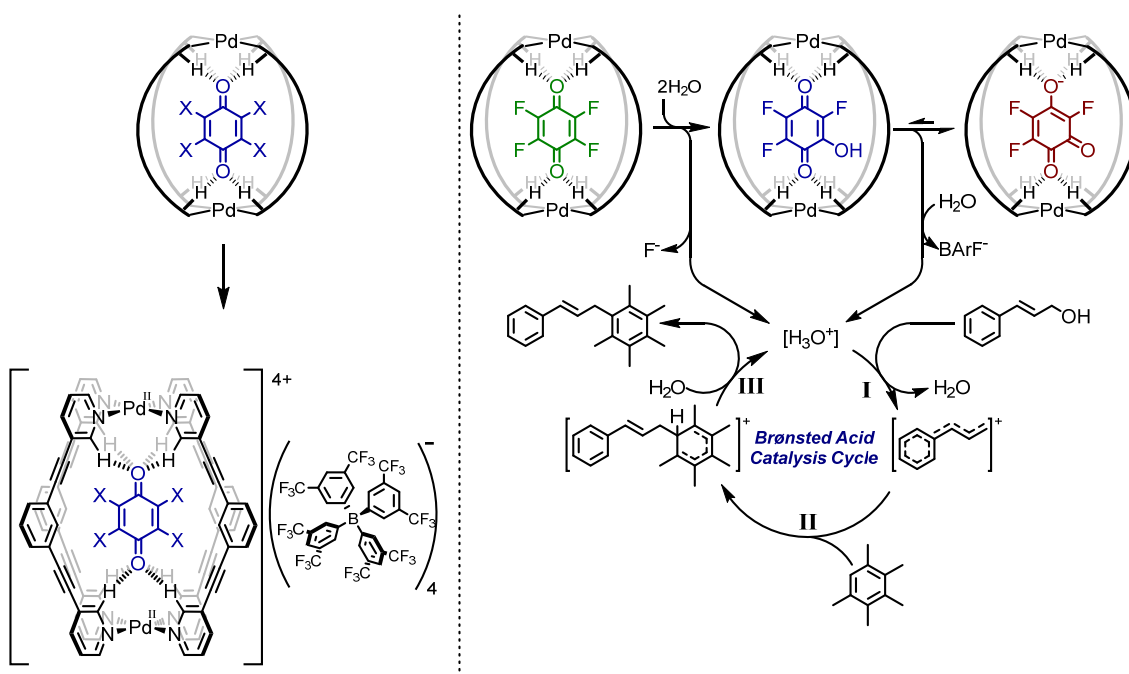
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Supramolecular catalysis using self-assembled coordination compounds as hosts is well established, with substrate encapsulation used to leverage a range of reactions and selectivities.¹ The most common hindrance to the turnover of these systems is the phenomenon known as product inhibition, where superior product binding precludes catalytic turnover.

The Lusby group has previously reported a supramolecular catalytic system that doesn't suffer from product inhibition using a Pd₂L₄ as a host for *p*-quinone compounds, activating them towards Diels-Alder cycloaddition with a wide range of dienes in organic solvents.² Due to their size-shape complementarity and strong hydrogen bonding with the Pd₂L₄ host, the electronics of the *p*-quinone guest can be drastically changed, resulting in a range of interesting reactivity possibilities.³

Herein we report our progress in a mechanistic study into the unprecedented reactivity of bound quinones as activatable powerful Brønsted acids for “exo-capsule” catalysis in bulk solution. Electron-deficient quinones are activated towards conjugate addition/elimination with water and resulting quinone-enols are significantly acidified through hydrogen bonding and strong ion pairing.



[1] C. Brown, F. Toste, R. Bergman and K. Raymond, *Chem. Rev.*, 2015, **115**, 3012-3035.

[2] V. Martí-Centelles, A. L. Lawrence and P. J. Lusby, *J. Am. Chem. Soc.*, 2018, **140**, 2862–2868.

[3] D. August, G. Nichol and P. J. Lusby, *Angew. Chem., Int. Ed.*, 2016, **128**, 15246-15250.